

Thin Film Li Ion Microbatteries for NASA Applications

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Rechargeable thin film microbatteries have recently become the topic of widespread research for use in low power applications such as battery-backed CMOS memory, miniaturized implantable medical devices and smart cards.¹ In particular, the Center for Integrated Space Microsystems (CISM) at NASA's Jet Propulsion Laboratory has interest in applying this technology for secondary power systems in miniaturized satellites, microsensors, microactuators and other remote MEMS applications. The general requirements of the microbatteries for these applications are high specific energy, wide range of temperature stability, low self-discharge rate, and flexibility of cell design. The thin film Li ion materials system using $\text{LiCoO}_2/\text{LiPO}_x\text{N}_{(1-x)}\text{SnO}$ is expected to fulfill these requirements.

A research group at Oak Ridge National Laboratory has recently reported high capacity, high cyclability, low self discharge rate for the microbattery using the $\text{LiCoO}_2/\text{LiPO}_x\text{N}_{(1-x)}\text{Li}$ materials system. This group has claimed more than 95% of the initial capacity was retained after nearly 40,000 cycles between 4.2 V and 3.0 V at a rate of $100 \mu\text{A}/\text{cm}^2$, a capacity of $60 \mu\text{Ah}/\text{cm}^2$ with negligible self discharge rates.² However, the Li anode in this cell poses numerous problems. First, the temperature tolerance of the cell is limited by the melting point of Li metal. Thus, for battery designs calling for vertical stacks of bipolar cells, the use of Li metal precludes annealing of LiCoO_2 cathode, essential to crystallize the as-deposited amorphous cathode films for desired electrochemical performance. Also, there is concern about the compatibility of Li with conventional microelectronic fabrication processes as well as obvious safety concerns.

The use of an alternative material to the Li anode has been investigated by many groups for both conventional and microbatteries. The SnO based systems show promise as a high capacity anode material, but suffer from poor cyclability due to mechanical damage to the anode following SnO reduction and subsequent Li alloying. This reduced cyclability of SnO is well documented for conventional batteries since first reported by Fujifilm Celltec. This behavior apparently extends to thin film anodes as well; the ORNL group reports considerably lower cycle life for the Si-Sn-O-N anode based microbatteries.³ Nonetheless, SnO based materials remain the most suitable alternative to metallic Li anodes.

Development of thin film microbatteries has begun at JPL with the goal of integration into power systems of near-term future robotic missions. Layers of LiCoO_2 have been deposited onto various substrates using rf magnetron sputtering. The as-deposited films show little electrochemical response in a prismatic cell with 1M $\text{LiPF}_6/1:1:1$ (DMC:EC:DEC) solution. However, upon annealing at 700°C for 1 hour, the films show cyclic voltammetry responses at 3.8 and 4.2 V, corresponding to a first order phase transition from LiCoO_2 to Li_xCoO_2 , and order-disorder transitions for delithiation of Li_xCoO_2 , respectively (Fig. 1).⁴ For the anode film studies, SnO

layers have been deposited onto Cu foil substrates via reactive sputtering of Sn in oxygen. These films can be cycled ~100 times before complete loss of capacity (Fig. 2). Also, $\text{LiPO}_x\text{N}_{(1-x)}$ films have been prepared by sputtering Li_3PO_4 in nitrogen, and suitable deposition parameters for these films have been established.

The purpose of this study is to characterize the $\text{LiCoO}_2/\text{LiPO}_x\text{N}_{(1-x)}\text{SnO}$ microbattery, with primary focus on the electrochemical properties of the SnO film. Cyclic voltammetry, EIS, and charge-discharge characteristics of the batteries will be presented. The behavior of the thin film SnO anodes compared to bulk SnO anodes in liquid electrolytes will be examined.

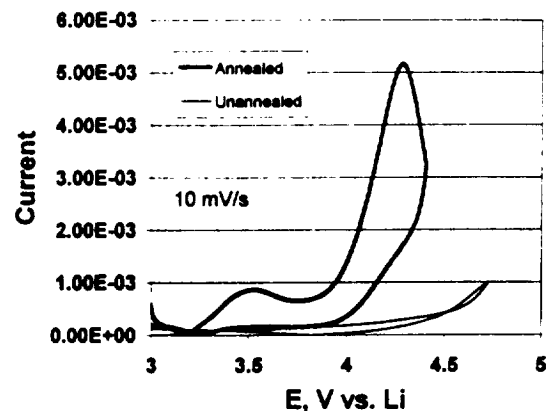


Fig. 1 Cyclic voltammetric data of annealed and unannealed LiCoO_2 films in 1 M $\text{LiPF}_6/\text{EC-DMC-DEC}$.

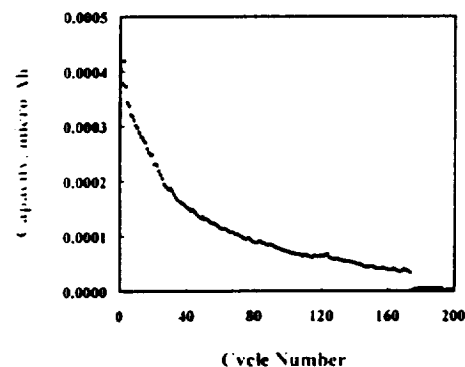


Fig. 2. Cycling behavior of SnO thin film anode (on Cu) in 1 M $\text{LiPF}_6/\text{EC-DMC-DEC}$ solution.

Acknowledgments

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References

- ¹See for example: J. B. Bates, N. J. Dudney, D. C. Lubben, G. R. Gruzalski, B. S. Kwak, Xiaohua Yu, and R. A. Zuhr, *J. Power Sources*, **54**, 58 (1995); P. Birke, W. F. Chu, and W. Weppner, *Solid State Ionics*, **93**, 1 (1997); S. D. Jones and J. R. Akridge, *J. Power Sources*, **54**, 63 (1995).
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